Application note

Positive material identification

Conducting Retroactive PMI Using Niton Handheld Analyzers

Introduction

Petroleum refining and its associated petrochemical industries are vital to the global economy, worth untold billions of dollars. This industry provides fuels and a host of products from plastics to fertilizers and consumables. Although refineries and petrochemical plants are among the most prized industrial assets globally, hydrocarbon processing is a high-hazard industry due to the nature of petrochemicals being processed and handled.

Worker health and safety continue to be the number one priority for the industry, with a particular focus on Process Safety Management (PSM) and asset integrity. Specific emphasis is placed on preventing releases (spills, etc.) of highly hazardous chemicals and toxic substances resulting in major accidents. Consequences of unintended releases could include fatal accidents and injuries, leaks, property loss, outages, and more.

Equipment failure is a primary cause of losses at refineries, chemical plants, pipeline networks, and gas processing facilities. Such failure can often be traced to the inadvertent or inappropriate substitution of construction materials, leading to potentially catastrophic consequences. Verifying the Mechanical Integrity (MI) of systems, piping, etc., is dependent on ongoing precise and accurate analysis of materials. Retroactive Positive Material Identification (PMI) using Thermo Scientific™ Niton™ XL5 Plus handheld XRF and Thermo Scientific™ Niton™ Apollo™ handheld LIBS analyzers ensures that critical system components in refineries are what they are supposed to be, identifying problems or inappropriate materials before failure happens.

Mechanical Integrity (MI) consistently remains a top-of-mind factor. Enforcement policies such as 29 CFR 1910.119 “Process Safety Management of Highly Hazardous Chemicals” issued by the United States Occupational Health and Safety Administration (OSHA) identify specific requirements geared towards minimizing and preventing catastrophic releases. OSHA’s National Emphasis Program (NEP) enacted specific policies to safeguard against potential catastrophes:

- **June 07, 2007:** Enforcement Directive Number CPL 03-00-004;
- **November 29, 2011**: Petroleum Refinery Process Safety Management National Emphasis Program and Directive Number CPL 03-00-014;

Application industry-reported data suggests a probability that approximately 3% of rogue material makes its way into the field. This rouge material often becomes a component of a final fabricated assembly, piping circuit, pressure vessel, or critical process equipment. The material may be used inadvertently by entering several point-of-entry scenarios including:

- Component manufacturer applies the incorrect material stamp to a finished part;
- Fabricator uses unmarked, unknown material during the fabrication process (i.e., loose stock, drops, cutouts);
- Multiple pieces are made from a single stock and material traceability is not maintained during fabrication (i.e., gussets, lift lugs, stiffener rings, support clips, pipe pups, gasket rings);
- Warehouse stocks inventory in the wrong location and error is carried forward;
- Welder uses incorrect filler metal due to selecting from wrong rod box, improper labeling or stocking of inventory, or borrowing weld rods from a fellow welder;
- Welder or pipefitter selects the wrong component during the fabrication process;
- Integrity of the original mill test report (MTR) is compromised during the procurement and supply cycle as ownerships exchanges and data is transposed or even manipulated;
- Maintenance occurring outside normal operating hours is not subjected to typical QA/QC inspection practice;
- Improper tagging or marking of materials during maintenance removal and lack of verification prior to re-installation.

The U.S. Chemical Safety and Hazardous Investigation Board (CSB) report No. 2005-04-B offers a lesson learned following an incident investigation into a major fire at one of the nation's largest refining complexes, which caused a reported $30 million in property damage and minor injuries.

Positive Material Verification Programs

In-situ alloy material verification using X-ray fluorescence (XRF), laser-induced breakdown spectrometry (LIBS), or other non-destructive material testing is an accurate, inexpensive, and fast Positive Material Identification (PMI) test method. Facility owners, operators, and maintenance contractors should ensure that verification programs require PMI testing to maximize safety. Appropriate verification programs include The American Petroleum Institute Recommended Practice (API RP) 578[1] or other suitable processes to verify all critical service alloy steel piping components removed and reinstalled during maintenance[2].

A study on petroleum refinery corrosion-related accidents in the European Union (EU) and Organization for Economic Cooperation and Development (OECD) countries reports that inadequacy of material composition was a critical component of failure in 9 of 99 significant refinery accidents. History reveals that inadvertent material substitutions continue to be a considerable problem in the refining and petrochemical industry. However, applying the principles and guidelines published in API RP 578 "Material Verification Program for New and Existing Alloy Piping Systems" supports utilizing Recognized and Generally Accepted Good Engineering Practices (RAGAGEP) when implementing an effective material verification program (MVP). Owner-users who adopt a thorough PMI practice for pressure-containing components, welds for in-service equipment, new construction materials, or during maintenance activities can significantly reduce the likelihood of material mix-up and avoid the consequences of failure while mitigating corporate risk.

Another area of concern is sulfidation corrosion and its effects on steel piping and equipment, a significant cause of leaks in the refining industry. When exposed to hydrocarbon containing sulfur compounds at elevated temperatures, carbon steels with low silicon content (sulfidation corrosion affects steel piping and equipment) are a substantial cause of leaks in the refining industry due to the carbon steels (<0.10%) accelerated corrosion rate. Sulfidation thins the pressure boundary wall resulting in an escape of highly hazardous chemicals into the atmosphere. API RP 939C "Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries" recognizes the implementation of Retrospective PMI into a material verification program (per API RP 578) as an inspection method to detect and track sulfidation corrosion.[3]

Moreover, HF alkylation is an increasingly central process in the refining industry to produce petrochemical products. With carbon steels being a principal material of construction like Monel™ 400, copper-nickel, and other nickel-based alloys such as Hastelloy™ C-276 and B-2, the proper selection, application, and placement of alloys within the process piping envelope is critical to avoid unexpected corrosion and deterioration of pressure equipment components. In the HF alkylation process, carbon steel has demonstrated satisfactory corrosion resistance to HF corrosion when residual element (RE) content is controlled. Case studies have shown that RE's in carbon steel can contribute to accelerated HF corrosion, primarily Cr, Ni, and Cu elements. A recognized guideline is that for base metal of C> 0.18 % wt % and Cu + Ni + Cr, 0.15 % wt % is optimum. These values are critical since the type and concentrations measured will directly affect the required analytical methods operations[4].

Handheld X-ray Fluorescence (HHXRF) is a fast and accurate non-destructive testing method that confirms alloy composition and positively identifies material grade according to specifications. HHXRF confirms the accuracy of purchased materials; assures QA/QC for in-process fabrication; meets end-user material requirements of outgoing products; and ensures installed components and welds match the engineering design and application for which they are intended.

The API 578 3rd edition also recommends Handheld Laser-Induced Breakdown Spectroscopy (HHLIBS) as a reliable method for PMI analysis. HHLIBS is a quick, accurate, and nearly non-destructive technique that measures the composition of alloys and identifies alloy grades. In the field, HHLIBS is used similarly to HHXRF, though the main difference stems from the HHLIBS carbon measurement capability. While HHXRF is easier to use for analyzing a larger variety of metals and alloys, HHLIBS is preferred when the measurement of carbon is critical to weldability or corrosion resistance of steel and stainless-steel assets. HHLIBS can differentiate steel and stainless-steel grades based on carbon concentration and calculate the carbon equivalency from the measured composition.

Niton XL5 Plus Handheld XRF Analyzer

The Niton XL5 Plus handheld XRF analyzer is the smallest and lightest high-performance HHXRF analyzer in the market. The Niton XL5 Plus analyzer reduces operator fatigue and enables testing access in spaces typically inaccessible to larger HHXRF, HHLIBS, and mobile Optical spectrometry (OES) equipment. The Niton XL5 Plus analyzer delivers fast, accurate elemental analysis ranging from Mg to Bi in demanding refinery environments and provides the refining industry with the following key benefits:

- Best in class analytical performance with proprietary 5W X-ray tube and state-of-the-art large silicon drift detector with a graphene window providing the overall highest precision, sensitivity, and fastest light element (Mg, Al, Si, P, and S) detection;
- Increased productivity with portability that enabling testing in tights spaces;
- Optimized user comfort with a lightweight design at 2.8 lbs (1.3 kg), suitable for rope access PMI inspection without operator fatigue;
- Equipped with an optional Kapton™ window and snap-in Hot Work Standoff to perform measurements at elevated temperatures under normal process operating conditions ranging from 200° F up to 900° F.

Niton Apollo Handheld LIBS Analyzer

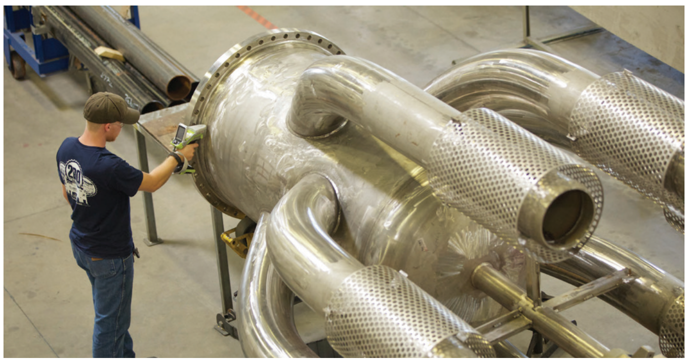
When knowledge of carbon content is essential, the Niton Apollo handheld LIBS analyzer is a reliable instrument for material analysis and critical asset inspection. Weighing just 6.4 lbs. (2.9 kg.), the Niton Apollo analyzer conveniently eliminates the need for bulky OES carts. Featuring a powerful, precise laser and high purity argon flush, the Niton Apollo analyzer provides PMI inspectors with various benefits:

- **Sealed argon purge** ensures superior signal stability, accurate measurement of chemical composition, and identification of steel and stainless-steel grades based on main alloy elements and carbon concentrations;
- Carbon measurement capability down to a 0.01% level accurately identifies L&H grades of stainless steel;
- Carbon equivalency calculation and real-time display determines the weldability of steel.

The Niton XL5 Plus analyzer and Niton Apollo analyzer are state-of-the-art instruments offering a smaller footprint and reduced weight burden compared to other HHXRF and mobile OES analyzers. Additional features include:

- Flexible interface enabling custom workflow solutions and easy optimization for specific applications like low silicon measurement, residual and trace element analysis, and carbon equivalency;
- Unparalleled chemistry and grade identification accuracy for precise results every time;

- Integrated 1.2M micro and 5M macro cameras and small spot analysis for accurate sample positioning, and image capture for improved reference and data integrity;
- Swiping, tilting, and vivid touch screen display that can be used even while wearing gloves;
- Rugged housing is splash and dustproof for harsh environments;
- Extended field use with hot-swappable battery and battery life indicator display.



Instrument selection for Material Verification Programs

Table 1 summarizes which instrument model is best suitable for your PMI program. In some cases, both technologies, HHXRF and HHLIBS, can and should be used.

Conclusion

Many challenges are associated with in-situ or retro-PMI testing to confirm that existing assets are fit for service in aging infrastructure. The Niton XL5 Plus analyzer and the Niton Apollo analyzer are designed and purpose-built to meet the requirements of process facility inspectors operating in all industry segments from refining and petrochemical to power generation, gas processing, and offshore and pipeline transportation. The Niton XL5 Plus analyzer is the ideal PMI tool offering best-in-class analytical performance, outstanding ergonomics, and mobility. While, the Niton Apollo analyzer complements the Niton XL5 Plus analyzer as a simple, maneuverable, and indispensable tool when identifying carbon concentration is critical is necessary.

Program	Application	Recommended Instrument(s)
API 578	General metal and alloy[a] PMI	Niton XL5 Plus
	P + S and main elementsb in low alloy steel	Niton XL5 Plus
	C and main elements[b] in carbon and low alloy steel	Niton Apollo
	C and main elements[b] in stainless steel for L/H grade	Niton Apollo
API RP 939 C	Sulfidic corrosion: measuring Low Si (<0.1%)	Niton XL5 Plus (needed on hot pipes) Niton Apollo
API RP 571	Residual elements: measuring low Cr+Cu+Ni (<0.15%)	Niton XL5 Plus Niton Apollo if C<0.18% needed

Table 1: Recommended instrument(s) for material verification

[a] All elements from Mg to Bi including and all type of alloys including low alloy steel, chromium steel, stainless steel, nickel, cobalt, copper, aluminum, titanium, tin, lead, magnesium, zirconium, tungsten alloys, etc.

[b] Main elements is steel and stainless steel, including Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu , Nb, Mo, W.

To learn more about sulfidation corrosion or identification of residual elements, visit www.thermofisher.com/oilandgas and read our latest application notes on these topics.

References

1. API RP 578 – Material Verification Program for New and Existing Alloy Piping Systems
2. "Safety Bulletin," U.S. Chemical and Safety Hazard Investigation Board, CSB report No. 2005-04-B, October 12, 2006, page 7.
3. API RP 939C – Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries
4. API RP 751 – Safe Operation of Hydrofluoric Acid Alkylation Units

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